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9705921.6

By virtue of a direction given unde. Section 30 of the Patents Act 1977, the application is proceeding in the name of

Coutaulds Packaging Limited
Mulberry House
Stephenson Road
Severalls Business Park
Colchester
Essex
CO4 4QR

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1. Your reference

PA97-03/MGS

2. Patent application number
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21 MAR 1997

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

1. COURTAULDS PACKAGING LIMITED
Mulberry House, Stephenson Road,
Severalls Business Park
Colchester, Essex, CO4 4QR
COURTAULDS plc
50 George Street, London, W1A 2BB

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

1. United Kingdom 2. United Kingdom

4. Title of the invention

LAMINATED MATERIALS AND CONTAINERS THEREFROM

5. Name of your agent *(if you have one)*

J.Y. & G.W. JOHNSON

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

KINGSBOURNE HOUSE
229-231 HIGH HOLBORN
LONDON WC1V 7DP

Patents ADP number *(if you know it)*

976001

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Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

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Number of earlier application	Date of filing *(day / month / year)*

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a) any applicant named in part 3 is not an inventor, or
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See note (d))

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Signature J.J.&G.W.J.S. Date 21.03.97

12. Name and daytime telephone number of person to contact in the United Kingdom Martin J NEWBY 0171 405 0356

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Laminated Materials and Containers Therefrom

Technical Field

This invention relates to laminated materials and to flexible containers formed from laminated materials, in particular thermoplastics laminates that include a layer of material having good vapour barrier properties.

Background of the Invention

Thermoplastics materials are widely used in packaging because of their low cost and ease of forming into a variety of shapes. However, most thermoplastics materials suffer from the disadvantage of providing only a relatively poor barrier to gases and vapours. Packaging having poor gas barrier properties is particularly disadvantageous for packaging oxygen-sensitive materials, such as foodstuffs, which are to be stored unrefrigerated. It is also disadvantageous for packaging to have poor vapour barrier properties when packaging items which are sensitive to moisture vapour, for example foodstuffs and confectionery which deteriorate when they become damp, and when packaging items which include flavouring components which diffuse through the packaging material with consequent loss of flavour.

Thermoplastic containers which are used for the storage and delivery of flavoured materials, e.g. toothpaste, are required to store the materials for prolonged periods of time e.g. up to three years, without substantial loss of flavouring.

It has generally been thought that loss of flavouring is due to two mechanisms, namely permeation and absorption. The loss of flavouring due to permeation has been ameliorated by the use of laminates containing barrier layers. A known thermoplastics material with good barrier properties is ethylene vinyl alcohol (EVOH) which is

typically used as a thin layer sandwiched between layers of other thermoplastics materials, typically polyolefinic materials. Other known materials with good barrier properties to vapour transmission are polyamides, polyacrylonitrile and aliphatic polyketones.

A typical prior art laminate having a centrally positioned barrier layer is shown in Figure 1 which will be described later.

Laminates having a barrier layer arranged asymmetrically within the different layers of the laminated material are also known. Figure 2, which will be described in detail later, shows a prior art laminated in which an EVOH barrier layer is arranged towards the inside surface, in use, of the laminate. The provision of such a barrier layer appears to reduce the loss of flavourings from within the container.

However, EVOH and other barrier layers materials are generally expensive and therefore a number of attempts have been made at improving the gas barrier properties of polyolefinic materials. GB-A-1136350, for example, proposes the use of circular plate-like fillers with a ratio of diameter to thickness of between 20:1 and 300:1 and a diameter of at most 40 μm in polyolefin polymers selected from polyethylene, polypropylene, ethylene-containing copolymers containing at least 50 moles percent of ethylene, and polystyrene, the preferred amount of filler being from 0.1 to 50 wt% of the total weight of filled polymer. Such filled polymer compositions have been proposed for the manufacture of films, for example films for food packaging.

US-A-3463350 is concerned with the production of moulded containers for packaging foodstuffs, the containers being made from mixtures of high density polyethylene (HDPE) and mica particles, for example by compression or injection moulding. Such containers are said to reduce the discolouration of so-called canned cornbeef as caused by oxygen compared with the use of similar containers made of

HDPE filled with glass fibre or titanium dioxide instead of mica.

It has also been proposed in US-A-4528235 to incorporate platelet filler particles with an average equivalent diameter of from 1 to 8 μm, the maximum diameter being 25 μm, and a thickness of less than 0.5 μm, into HDPE having a melt index of from 0.01 to 1.0 g/10 minutes at 190°C as measured by ASTM D-1238 to produce films having a thickness of from 10 to 100 μm, with the intention of increasing the effectiveness of the barrier to oxygen of the films compared with films formed from unfilled HDPE.

In WO-A-96/17885, the contents of which are hereby incorporated into the present invention, there is proposed a moulding composition, and a method of making a moulding composition, for forming an article having increased barrier to gases and/or vapours, the method comprising the step of mixing together a substantially non-polar thermoplastics resin and a laminar filler, the laminar filler being capable of delaminating when the composition is subjected to high shear to increase the aspect ratio of the filler as it breaks down into platelets. WO-A-96/17885 further describes a composition containing 85 parts by weight of high density polyethylene and 15 parts by weight of talc that can be extruded in the form of a film or tube having increased barrier properties. The composition can be extruded as a single web, or can be co-extruded with other layers of material formed on one or other side of a core layer formed from the composition.

Disclosure of the Invention

The object of the present invention is to provide a laminated material which is relatively cheap and which has good resistance to the loss of flavour in goods stored in a container formed from the material.

According to one aspect of the present invention there is provided a method of reducing the absorbability of a laminated material used for the manufacture of flexible containers and which in use has an intended inner surface and an impermeable core barrier layer, comprising arranging for a further layer, formed from substantially non-polar thermoplastics resin or material filled with a platelet filler, to be positioned inwardly of the barrier layer.

The platelet filler can be any of a variety of lamellar fillers provided the platelets delaminate under shear when the filler is blended with the non-polar thermoplastics resin before processing and more particularly when the mixture of filler and thermoplastics resin is subjected to extrusion. Lamellar fillers include clays, mica, graphite, montmorillonite and talc.

Talc is a particularly preferred lamellar filler by virtue of its ease of delamination during shear. Talc, being a naturally occurring hydrated magnesium silicate, is available in a variety of grades of greater or lesser purity. It has been found that the ease of increasing the aspect ratio of talc when it is subjected to high shear in a non-polar thermoplastics resin appears to increase as the level of impurities within the talc decreases. Thus not only does it appear easier to delaminate the platelets of the talc, but the platelets themselves apparently resist fracture. Thus purer grades of talc are generally preferred since they lead to compositions which not only have good barrier properties but also have a high degree of whiteness without the necessity to include a white pigment such as titanium dioxide.

According to another aspect of the present invention, there is provided a laminated material for the manufacture of flexible containers and which, in use, has a surface intended to be external of the container and a surface intended to be internal of the container, the laminated material comprising an intermediate barrier layer of a

thermoplastics material having, on its inner side, a further layer comprising substantially non-polar thermoplastics resin filled with platelet filler, preferably high purity talc.

The preferred non-polar thermoplastics resin is a polyolefin resin, for example a polymer derived from one or more aliphatic or aromatic alkylenes, e.g. a polymer containing units derived from at least one of ethylene, propylene, butylene, styrene, hexene and octene. The non-polar resin may also comprise a compound of one or more polymers as detailed below. Examples of specific polyolefin resins which can be used include polyethylene, polypropylene, ethylene/propylene copolymers, ethylene/propylene/butylene terpolymers, polyethylenes being particularly preferred by virtue of their good processing and welding characteristics. The polyethylene can be low density polyethylene (density of from 0.910 to 0.925 $g.cm^{-3}$) linear low density polyethylene, medium density polyethylene (density of from 0.925 to 0.950 $g.cm^{-3}$), linear medium density polyethylene or high density polyethylene (density of from 0.950 to 0.980 $g.cm^{-3}$). High density polyethylene, or a compound of high density polyethylene and linear low density polyethylene, is particularly preferred by virtue of its higher inherent barrier properties compared with lower density polyethylenes.

The preferred HDPE resin has a density of at least 0.945 $g.cm^{-3}$ and a melt flow index of 4-10 g/10 min preferably 7 to 8 g/10 min, (2160 g load at 190°C) measured to ISO/IEC 1133. A suitable material is available from DSM grade 9089F.

Particularly preferred grades of talc for use in the present invention are sold by Richard Baker Harrison Group, England under the Trade Mark MAGSIL, and an especially preferred grade is "Magsil Osmanthus" which delaminates in processing to form platelets having an average aspect ratio of from 16-30 and a minimum aspect ratio of 5.

Since the purity of talc is related to its whiteness, the preferred talc forms a moulded composition, as described below, having a CIE whiteness index of at least 40. These CIE (Commission Internationale d'Eclairage) whiteness index values are determined for compositions containing 15 percent by weight of talc in high density polyethylene with no other filler present, the determination being in reflectance mode with UV light included and specular reflection excluded, the observer angle being 10° and the samples being backed by a white tile.

The talc is blended with the polyethylene in the weight ratio of 15 parts to 85 parts of polymer using a twin screw extruder or Banbury type mixer with a temperature profile ranging from 150°C to 220°C, the mixture being subjected to high shear during mixing, and then being extruded and cut into pellets. The pellets are then compression moulded to form plaques at a temperature of 150° and pressure of 0.39 tonnes for 5 minutes.

The CIE whiteness index is measured using a Macbeth Spectrophotometer 2020+.

According to a further aspect of the present invention there is provided a container having flexible walls formed from a laminated material having a core barrier layer of a thermoplastics material with at least one further layer arranged internally of the barrier layer, said one further layer comprising substantially non-polar thermoplastics resin filled with platelets of talc having an aspect ratio of at least 5, an average aspect ratio of from 16-30 and a CIE whiteness of at least 40.

The arrangement of a layer of talc-filled non-polar thermoplastics resin internally of the barrier layer enables the thickness of the thermoplastics barrier layer to be reduced, from typically 25 microns, to a thickness of from between 5 to 15 microns, preferably 10 microns, without substantially affecting the overall losses of volatiles from

within the container. This is because the absorption properties of the container wall material are improved, that is less material is absorbed, whilst the permeation rate through the thinned down barrier layer remains largely unchanged.

The laminate construction can be a substantially symmetrical construction with the barrier layer at the centre and a layer comprising non-polar thermoplastics resin filled with platelet filler being arranged both inside and outside of the barrier layer. This allows the laminate to be used either way round which has advantages in the production of containers.

Preferably the thermoplastics barrier layer is an ethylene vinyl alcohol material or amorphous polyamide material. Preferably the talc filled non-polar thermoplastics resin layer has a thickness of from between 5-150 microns, preferably 10-70 microns, more preferably about 50 microns, and is spaced from the barrier layer only by a tie layer.

Preferably the talc filled non-polar thermoplastics resin layer is spaced from the internal surface of the laminate by an additional inner layer of a non-polar thermoplastics resin in order to improve the weld characteristics of the laminate on its inner surface.

Preferably the further layer is a high density polyethylene compound which may contain 15% by weight of talc filler, and at least a major, i.e. in excess of 50%, portion of high density polyethylene.

Brief Description of Drawings

The invention will now be described, by way of example only, and with reference to the accompanying drawing, in which:-

Figure 1 and Figure 2 are schematic representations of prior art laminates;

Figure 3 is a schematic representation of a control laminate; and

Figure 4 is a schematic representative of a laminate according to the present invention.

Detailed Description of the Invention

Sample 1

A known laminate 11, illustrated in Figure 1, has an overall thickness T of about 300 microns and comprises a plurality of layers 12-20, the inner layer being identified layer 12 and the external layer being layer 20. The inner layer 12 comprises linear medium density polyethylene (LMDPE) having a thickness of about 75 microns, and the adjacent outer layer 13 comprises low density polyethylene (LDPE) having a thickness of about 20 microns. Externally of the layer 13 is a layer 14 of linear low density polyethylene (LLDPE) having a thickness of about 20 microns which is adhered to an ethylene vinyl alcohol (EVOH) barrier layer 16 (shaded for ease of identification) by a tie layer 15. The tie layer 15 typically comprises a maleic anhydride functionalised polyethylene of about 5 microns thickness and the barrier layer 16 has a thickness of about 25 microns.

Externally of the barrier layer 16 are a tie layer 17, a LLDPE layer 18 and a LDPE layer 19 which are substantially identical to the layers 15, 14 and 13, respectively. The external layer 20 is a layer of medium density polyethylene (HDPE) having a thickness of about 110 microns.

Sample 2

The second prior art laminate 21 shown in Figure 2 again has an overall thickness T of about 300 microns and

comprises a plurality of layers 22-28, the inner layer being layer 22 and the external layer being layer 28. The inner layer 22 comprises LMPDE having a thickness of about 35 microns which is adhered to an EVOH barrier layer 24 (shaded for ease of identification) by a tie layer 23. The EVOH barrier layer 24 is about 15 microns thick and the tie layer 23 has a thickness of about 5 microns. Externally of the barrier layer 24 is another tie layer 25, a layer 26 of LLDPE having a thickness of 20 microns, a layer 27 of LLDPE or LDPE having a thickness of about 110 microns, and the external layer 28 of medium density polyethylene (MDPE) also having a thickness of about 110 microns.

Sample 4

A laminate 41 according to the invention is shown in Figure 4 and has an overall thickness T of about 175 microns and comprises a plurality of layers 42-48, the inner layer being layer 42 and the outer layer being layer 48. The inner layer 42 comprises LMPDE having a thickness of about 25 microns. The adjacent outer layer 43 comprises talc-filled HDPE which is adhered to a barrier layer 45 by a tie layer 44 having a thickness of about 7.5 microns. The barrier layer 45 may be EVOH or an amorphous polyamide and has a thickness of about 10 microns. In the sample tested the layer comprises amorphous polyamide. The laminate is arranged so that the different layers are arranged symmetrically on each side of the barrier layer 45. Externally of the barrier layer 45 is a further tie layer 46, a talc-filled HDPE layer 27 and an LHDPE layer 48. The layers 46-48 are, respectively, identical to the layers 44, 43, 42 so that the laminate is symmetrical around the barrier layer 45.

Sample 3

A control laminate 31 is shown in Figure 3 and has an overall thickness T of about 275 microns. The laminate 31 from inside to outside comprises layers 32-38. The inner

layer 32 is a layer of LMPDE about 25 microns thick. The adjacent outer layer 33 is HDPE with a thickness of 50 microns which is adhered to an EVOH barrier layer 35 by a tie layer 34. The barrier layer 35 is about 10 microns thick and the tie layer 34 has a thickness of 7.5 microns. Externally of the barrier layer 35 is a second tie layer 36, an outer HDPE layer 37 having a thickness of 150 microns, and an external LHPDE layer 38 having a thickness of about 25 microns.

Absorption Tests

The laminate material samples 1 to 4 were hermetically sealed across the mouths of 500 ml jars each containing a flavouring from the following: limonene, cineole, menthone and carvone. The mouths of the jars had a diameter of 48 mm to give an exposed area of laminate of 0.0072 m^2. The jars were maintained at a temperature of 25°C and at atmospheric pressure. The laminate samples were weighed periodically and the maximum absorption for all flavourings reached a substantially steady state after 7 days (168 hours).

The results of the tests are given in the tables below in Table 1.

Table 1

Absorption as weight gain per square meter after 7 days

Flavouring	Sample 1	Sample 2	Sample 3	Sample 4
limonene	2.3611	0.98611	2.8055	1.3472
cineole	2.1388	1.0833	2.4861	1.1388
menthone	1.3333	0.6805	1.8194	0.8888
carvone	0.8611	0.2500	1.2083	0.6527

The results for Samples 1 and 2 demonstrate that the placement of the barrier layer 24 closer to the inside

surface of the laminate as in Sample 2 is beneficial even though the thickness of the barrier layer 24 has been reduced in comparison to that of the barrier layer in Sample 1, and the overall thickness of the laminate remains the same.

It can be seen that Sample 4, which is the sample according to the invention, has unexpectedly good absorption properties in that the barrier layer 45 in Sample 4 is spaced 82.5 microns from the internal surface of the laminate, which distance is identical to the spacing of the barrier layer 35 from the internal surface of the laminate of Sample 3. The improvement in absorption properties is due to the replacement of the HDPE layer 33, in Sample 3, with the talc-filled HDPE layer 43 of Sample 4.

The talc-filled layer 43, which is inside the barrier layer 45, helps reduce the weight loss of flavouring due to absorption into the laminate. The talc-filled layer should be from between 5-150 microns in thickness, preferably from about 18-70 microns and more preferably about 50 microns in thickness. The talc-filled layer also tends to stiffen the laminate allowing a laminate of reduced overall thickness to be used whilst still maintaining a relatively stiff material.

CLAIMS

1. A method of reducing the absorbability of a laminated material used for the manufacture of flexible containers and which in use has an intended inner surface and an impermeable core barrier layer, said method comprising the arranging for a further layer, formed from substantially non-polar thermoplastics resin filled with a platelet filler, to be positioned inwardly of the barrier layer.

2. A method according to claim 1, wherein the platelet filler comprises a high purity talc.

3. A method according to claim 1 or 2, wherein said further layer is adjacent the barrier layer and is adhered thereto by a tie layer.

4. A method according to any one of claims 1 to 3, wherein, in order to aid welding of the laminated material, the further layer is spaced from the inner surface of the laminated material by an additional layer of non-polar thermoplastics resin material.

5. A laminated material for the manufacture of flexible containers and which, in use, has a surface intended to be external of the container and a surface intended to be internal of the container, the laminated material comprising an intermediate barrier layer of thermoplastics material having, on its inner side, a further layer comprising substantially non-polar thermoplastics resin filled with platelet filler.

6. A laminated material according to claim 5, wherein the platelet filler comprises high purity talc.

7. A laminated material according to claim 5 or 6, wherein the further layer has a thickness of between 20 and 150 microns, preferably about 50 microns.

8. A laminated material according to any one of claims 5 to 7, wherein said further layer comprises high density polyethylene, or at least a major portion of high density polyethylene.

9. A laminated material according to claim 8 when dependent upon claim 6, wherein said further layer comprises between 5-30% by weight of talc.

10. A laminated material according to any one of claims 5 to 9, wherein said further layer is spaced from the internal surface of the laminated material by an additional layer of non-polar thermoplastics resin material.

11. A laminated material according to any one of claim 5 to 10, wherein said barrier layer has a thickness of between 5-25 microns, and said further layer has a thickness of about 50 microns.

12. A flexible container having walls formed from a laminated material as claimed in any one of claims 5 to 11.

13. A flexible container having flexible walls formed from a laminated material having a core barrier layer of a thermoplastics material with at least one further layer arranged internally of the barrier layer, said one further layer comprising substantially non-polar thermoplastics resin filled with platelets of talc having an aspect ratio of at least 5, an average aspect ratio of 16-30 and a CIE whiteness of at least 40.

FIG. 1

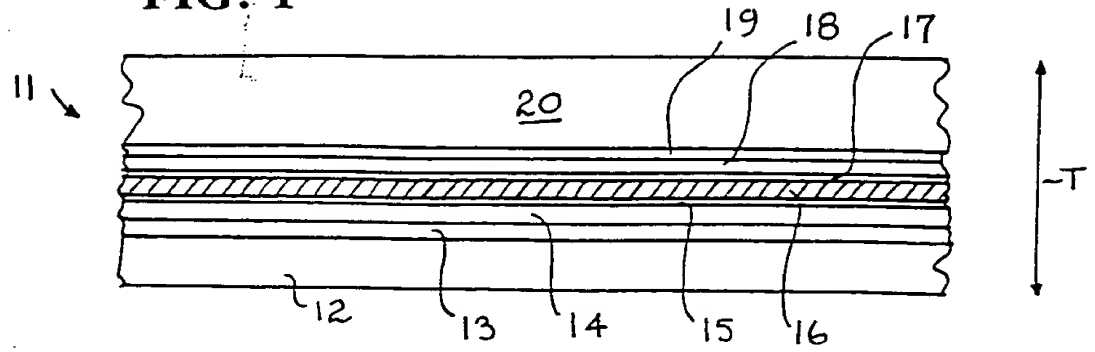

FIG. 2

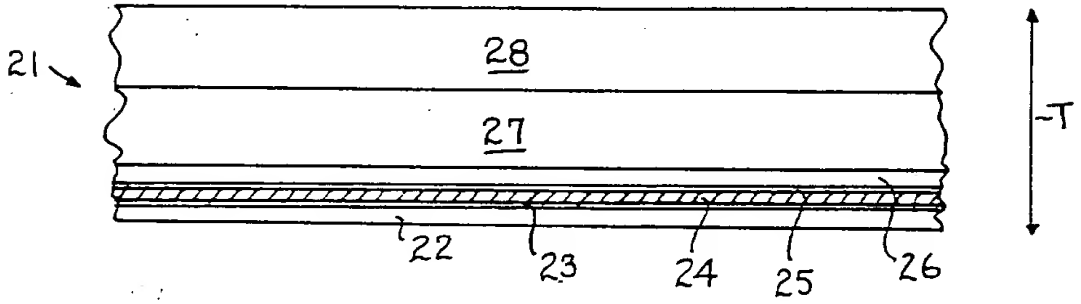

FIG. 3

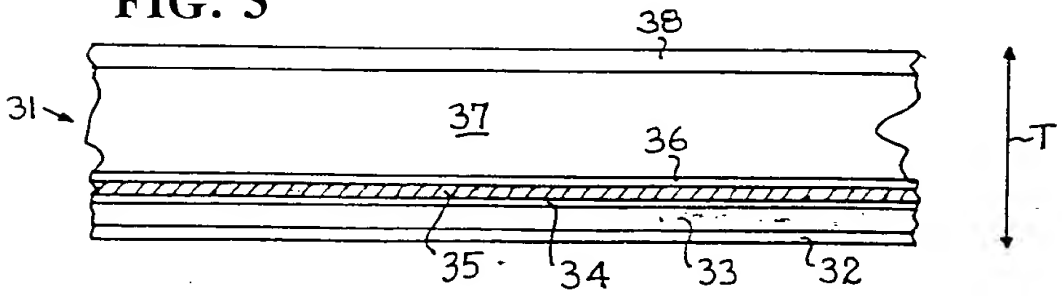

FIG. 4